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(54) **MÉTHODE POUR PRÉPARER DES POLYURETHANES
THERMOPLASTIQUES**
(54) **PROCESS FOR THE PREPARATION OF THERMOPLASTIC
POLYURETHANES**

(57) Dans un procédé pour préparer des polyuréthanes thermoplastique par réaction (a) d'isocyanates avec (b) des composés réactifs vis-à-vis des isocyanates et possédant une masse molaire de 500 à 10 000 g/mole, en présence ou non (c) d'extenseurs de chaîne de masse molaire inférieure à 500 g/mole, (d) de catalyseurs et (ou) (e) de produits auxiliaires et d'additifs usuels, le constituant (b) utilisé comprend au moins un polyéther-polyalcool (b1) à base d'unités de polyoxypropylène et de polyoxyéthylène, avec une masse molaire de 500 à 10 000 g/mole, un taux d'insaturation inférieur à 0.07 meq/g et une teneur de 80 à 100 % en groupes hydroxyle primaire.

(57) In a process for preparing thermoplastic polyurethanes by reacting (a) isocyanates with (b) compounds reactive toward isocyanates and having a molecular weight of from 500 to 10,000 g/mol, in the presence or absence of (c) chain extenders having a molecular weight of less than 500 g/mol, (d) catalysts and/or (e) customary auxiliaries and additives, the component (b) used comprises at least one polyether polyalcohol (b1) comprising polyoxypropylene and polyoxyethylene units and having a molecular weight of from 500 to 10,000 g/mol, an unsaturation of less than 0.07 meq/g and a primary hydroxyl group content of from 80 to 100 %.

Abstract

In a process for preparing thermoplastic polyurethanes by reacting (a) isocyanates with (b) compounds reactive toward isocyanates and having a molecular weight of from 500 to 10,000 g/mol, in the presence or absence of (c) chain extenders having a molecular weight of less than 500 g/mol, (d) catalysts and/or (e) customary auxiliaries and additives, the component (b) used comprises at least one polyether polyalcohol (b1) comprising polyoxypropylene and polyoxyethylene units and having a molecular weight of from 500 to 10,000 g/mol, an unsaturation of less than 0.07 meq/g and a primary hydroxyl group content of from 80 to 100 %.

We claim:

1. A process for preparing thermoplastic polyurethanes by reacting (a) isocyanates with (b) compounds reactive toward isocyanates and having a molecular weight of from 500 to 10,000 g/mol, in the presence or absence of (c) chain extenders having a molecular weight of less than 500 g/mol, (d) catalysts and/or (e) customary auxiliaries and additives,
5 wherein the component (b) used comprises at least one polyether polyalcohol (b1) comprising polyoxypropylene and polyoxyethylene units and having a molecular weight of from 500 to 10,000 g/mol, an unsaturation of less than 0.07 meq/g and a primary hydroxyl group content of from 80 to 100 %.
- 15 2. A process as claimed in claim 1, wherein the polyether polyalcohol (b1) contains from 5 to 30 % by weight of polyoxyethylene units, based on the total weight of all the polyoxyalkylene groups.
- 20 3. A process as claimed in claim 1 or 2, wherein the component (b1) has a hydroxyl number of from 10 to 230 mg KOH/g.
- 25 4. A process as claimed in any of claims 1 to 3, wherein the component (b1) has a functionality of from 1.9 to 3.0.
5. A process as claimed in any of claims 1 to 4, wherein the polyol component (b) comprises polytetrahydrofuran in addition to the polyether polyalcohols (b1).
- 30 6. A thermoplastic polyurethane obtainable by a process as claimed in any of claims 1 to 5.
- 35 7. A polyol component comprising
from 30 to 90 %
by weight of polyether polyalcohol comprising polyoxypropylene and polyoxyethylene units and having a molecular weight of from 500 to 10,000 g/mol, an unsaturation of less than 0.07 meq/g and a primary hydroxyl group content of from 80 to 100 %, and also
40 from 10 to 70 %
45 by weight of polytetrahydrofuran.

8. A method of using polyether polyalcohols comprising polyoxypropylene and polyoxyethylene units and having a molecular weight of from 500 to 10,000 g/mol, an unsaturation of less than 0.07 meq/g and a primary hydroxyl group content of from 80 to 100% for preparing thermoplastic polyurethanes.

PROCESS FOR THE PREPARATION OF THERMOPLASTIC POLYURETHANES

The present invention relates to a process for preparing thermoplastic polyurethanes by reacting (a) isocyanates with (b) compounds reactive toward isocyanates and having a molecular weight of from 500 to 10,000 g/mol, in the presence or absence of (c) chain extenders having a molecular weight of less than 500 g/mol, (d) catalysts and/or (e) customary auxiliaries and additives, and 10 also the thermoplastic polyurethanes which can be prepared by this process. Furthermore, the invention relates to polyol components which comprise at least one polyether alcohol comprising polyoxypropylene and polyoxyethylene units and having a molecular weight of from 500 to 10,000 g/mol, an unsaturation of less than 15 0.07 meq/g and a primary hydroxyl group content of from 80 to 100 % plus polytetrahydrofuran.

Thermoplastic polyurethanes, hereinafter also referred to as TPUs, are partially crystalline materials and belong to the class 20 of thermoplastic elastomers. They have a combination of advantageous material properties such as low abrasion, good chemical resistance and simultaneously high flexibility and high strength with the advantages of inexpensive thermoplastic processing which can be carried out continuously or batchwise by various known 25 methods, for example the belt or extrusion process. An overview of TPUs, their properties and applications is given, for example, in "Kunststoff-Handbuch", volume 7, Polyurethane, 3rd edition, 1993, edited by G. Oertel, Carl Hanser Verlag, Munich.

30 To prepare TPUs, use is customarily made of polytetrahydrofurans (PTHFs) having molecular weights of from 500 to 2000 g/mol as polyether polyalcohols, hereinafter also referred to as polyols. The use of polypropylene glycols having molecular weights of from 35 1000 to 4000 g/mol to which terminal ethylene oxide units have been added in order to obtain primary hydroxyl groups are described for the preparation of TPUs in, for example, US 5 185 420 and WO 93/24549. The polyether polyols described in these documents by way of example, which contain 70 or 75.6 % of primary hydroxyl groups, have the disadvantage of unsatisfactory reactivity toward 40 isocyanates so that an undesirably high catalyst concentration is required for a reaction in the one-shot process.

In addition, the TPUs prepared using these polyols have considerable disadvantages in their mechanical properties compared with 45 the TPUs based on PTHF.

It is an object of the present invention to develop a process for preparing thermoplastic polyurethanes having an improved reactivity of the polyol component, where the TPUs prepared by the process should also have an improved mechanical property profile 5 compared with the previously known TPUs based on polypropylene glycols.

We have found that this object is achieved in the preparation of thermoplastic polyurethanes by reacting (a) isocyanates with (b) 10 compounds reactive toward isocyanates and having a molecular weight of from 500 to 10,000 g/mol, in the presence or absence of (c) chain extenders having a molecular weight of less than 500 g/mol, (d) catalysts and/or (e) customary auxiliaries and additives, using a component (b) which comprises at least one 15 polyether polyalcohol (b1) comprising polyoxypolypropylene and polyoxethylene units and having a molecular weight of from 500 to 10,000 g/mol, an unsaturation of less than 0.07 meq/g and a primary hydroxyl group content of from 80 to 100 %.

20 The novel polyols of the component (b1) have an unsaturation of less than 0.07 meq/g, preferably from 0.001 to 0.05 meq/g, particularly preferably from 0.001 to 0.04 meq/g, in particular from 0.001 to 0.01 meq/g. The unsaturation which is customarily given in meq per g of polyether polyalcohol can be determined by generally known methods, for example by the known Kaufmann method by bromination of the double bonds and subsequent iodometric titration. The unit meq/g generally corresponds to the double bond content in mmol per g of polyether polyalcohol. The molecular weight of the polyols (b1) is from 500 to 10,000 g/mol, preferably from 1000 to 5000 g/mol, particularly preferably from 1000 to 2750 g/mol.

30 The hydroxyl number of the polyols (b1) is generally from 10 to 230 mg KOH/g. The polyols preferably have a hydroxyl number of from 52 to 110 mg KOH/g, particularly preferably from 60 to 100 mg KOH/g. The functionality of the polyols is dependent on the unsaturation of the polyols and the functionality of the initiator molecules. For the preparation of thermoplastic polyurethanes, the functionality is preferably from 1.9 to 3.0, particularly preferably from 1.95 to 2.8, in particular from 1.95 to 2.2, since a higher functionality leads to crosslinked polyurethanes which make thermoplastic processing difficult.

40 The polyols (b1) of the present invention can be prepared, for example, according to generally known methods by alkoxylation of initial substances which preferably have a functionality of 2 with alkylene oxides in the presence of, for example, basic salts

of cesium, e.g. cesium hydroxide, and/or basic salts and/or hydroxides of alkaline earth metals as catalysts. The catalysts used in the alkoxylation are preferably cesium hydroxide and/or calcium hydroxide.

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As initiator substances, preference is given to using difunctional substances such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, diols of butane, for example 1,4-butanediol, polyoxyethylene glycols and/or preferably polyoxypropylene glycols having customary molecular weights of less than 500 g/mol. Higher-functional initiator substances such as glycerol and/or trimethylpropane can be used as initiator substances, with the functionality of the novel polyols (b1) prepared preferably being in the range indicated.

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The polyols (b1) of the present invention comprise both polyoxyethylene and polyoxypropylene units. A preferred embodiment can be carried out, for example, by sufficient addition of propylene oxide to the initiator substances so as to synthesize a block of polyoxypropylene units having a molecular weight of preferably at least 700 g/mol, particularly preferably at least 900 g/mol. This preferred block of polyoxypropylene units can either be added directly onto the initiator substances or alternatively onto alkylene oxides which have already been added onto the initiator substances. For example, the initiator substances can first be alkoxylated with further alkylene oxides, for example butylene oxide and/or preferably ethylene oxide, and subsequently as described with propylene oxide, or else first with propylene oxide and subsequently with further alkylene oxides, for example butylene oxide and/or preferably ethylene oxide. However, the polyoxypropylene block is preferably added directly onto the initiator substances. Furthermore, the initiator substance can be alkoxylated with further alkylene oxides, for example butylene oxide and/or preferably ethylene oxide, together with propylene oxide.

Preference is given to using polyols which contain from 5 to 30 % by weight, particularly preferably from 15 to 25 % by weight, in particular from 15 to 22 % by weight, of polyoxyethylene groups, based on the total weight of all the polyoxyalkylene groups.

Preferably, the polyols are finally alkoxylated with ethylene oxide, as a result of which the polyols (b1) have terminal polyoxyethylene groups. Particular preference is given to block polymers in which first propylene oxide and then, in a second stage, ethylene oxide are added onto the initiator substance. The proportion of terminal polyoxyethylene units in the polyols (b1) of

the present invention is preferably from 5 to 30 % by weight, particularly preferably from 5 to 25 % by weight, based on the total weight of all the polyoxyalkylene groups. The proportion of primary hydroxyl groups in the polyols (b1) is, according to the 5 present invention, from 80 to 100 %, preferably from 82 to 95 %.

The preparation of polyols (b1) of the present invention may, for example, be carried out as follows:

10 The initiator substances and the catalysts can, preferably after removing any water present at elevated temperature and reduced pressure, be reacted with propylene oxide and possibly further alkylene oxides in a customary reactor or autoclave, for example a stirred reactor or a tube reactor fitted with customary facilities for cooling the reaction mixture. The catalyst is usually present in the reaction mixture in an amount from 0 to 10 ppm, based on the total formulation. The alkoxylation is preferably carried out at a temperature of the reaction mixture within a range from 70°C to 150°C, particularly preferably from 80°C to 15 105°C. The reaction is carried out at generally known pressures. The alkylene oxides can, as a rule, be added to the reaction mixture over a period of from 4 to 20 hours, depending on the desired molecular weight of the polyol. Preferably, the propylene oxide is added at the beginning of the reaction so that, as described, a block of polyoxypropylene units having a molecular weight of at least 700 g/mol is added onto the initiator substances. The reaction time can be from 1 to 8 hours, with complete reaction of the alkylene oxides preferably being ensured. After 20 complete conversion of the, for example, propylene oxide and possibly further alkylene oxides, polyoxyethylene units are subsequently particularly preferably added onto the end of the polyol by addition of ethylene oxide. Subsequently, the reaction mixture is, as a rule, cooled, preferably under reduced pressure, and worked up in a known manner. For example, the cesium catalyst can 25 be removed from the polyol by adsorption on, for example, silicates and subsequent filtration. Alternatively, the basic catalyst salts, for example the hydroxides mentioned, can be neutralized, e.g. by a suitable acid such as phosphoric acid, and left in the polyol. Known stabilizers, e.g. against oxidation, can subsequently 30 be added to the polyols.

In addition to the polyol component (b1) of the present invention, it is possible to use, if desired, further compounds reactive toward isocyanates, for example polyether polyols and/or 45 polyester polyols, which can have a customary unsaturation of greater than 0.07 meq/g, and/or, for example, PTHF. The proportion by weight of the polyols of the present invention based on

the total weight of all the isocyanate-reactive compounds used in the preparation of the TPUs, ie. the sum of the components (b) and (c), is preferably at least 0.1 % by weight, preferably from 0.1 to 90 % by weight, particularly preferably from 30 to 90 % by weight, in particular from 40 to 80 % by weight. Preference is given to using a polyol component (b) which comprises both PTHF and the polyols (b1) of the present invention. Particular preference is given to a polyol component comprising from 30 to 90 % by weight, in particular from 40 to 80 % by weight, of polyether 10 polyalcohol having a molecular weight of from 500 to 1000 g/mol, an unsaturation of less than 0.07 meq/g and from 80 to 100 % of primary hydroxyl groups plus from 10 to 70 % by weight, in particular from 20 to 60 % by weight, of polytetrahydrofuran.

15 The components (a), (b) and, if desired, (c), (d) and/or (e) customarily used in the preparation of the TPUs are described below by way of example:

- a) suitable organic isocyanates (a) are preferably aliphatic, 20 cycloaliphatic and in particular aromatic diisocyanates. Specific examples are: aliphatic diisocyanates such as hexamethylene 1,6-diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 2-ethylbutylene 1,4-diisocyanate or mixtures of at least 2 of the C₆-alkylene diisocyanates mentioned, penta- 25 methylene 1,5-diisocyanate and butylene 1,4-diisocyanate, cycloaliphatic diisocyanates, such as 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), cyclohexane 1,4-diisocyanate, 1-methylcyclohexane 2,4- and 2,6-diisocyanate and also the corresponding isomer 30 mixtures, dicyclohexylmethane 4,4'-, 2,4'- and 2,2'-diisocyanate and also the corresponding isomer mixtures and preferably aromatic diisocyanates, such as tolylene 2,4-diisocyanate, mixtures of tolylene 2,4- and 2,6-diisocyanate, diphenylmethane 4,4'-, 2,4'- and 2,2'-diisocyanate (MDI), 35 mixtures of diphenylmethane 2,4'- and 4,4'-diisocyanate, urethane-modified liquid diphenylmethane 4,4'- and/or 2,4'-diisocyanates, 4,4'-diisocyanato(1,2-diphenylethane) and naphthylene 1,5-diisocyanate. Preference is given to using hexamethylene 1,6-diisocyanate, dicyclohexylmethane 40 4,4'-diisocyanate, isophorone diisocyanate, diphenylmethane-diisocyanate isomer mixtures having a diphenylmethane 4,4'-diisocyanate content of greater than 96 % by weight and in particular diphenylmethane 4,4'-diisocyanate.
- 45 b) In addition to the above-described polyols (b1) of the present invention, isocyanate-reactive substances (b) which can be used are, for example, polyhydroxyl compounds having mole-

5 cular weights of from 500 to 10,000, preferably polyetherols and polyesterols. However, hydroxyl-containing polymers, for example polyacetals such as polyoxymethylene and especially water-insoluble formals, e.g. polybutanediol formal and poly-
10 hexanediol formal, and aliphatic polycarbonates, particularly those prepared from diphenyl carbonate and 1,6-hexanediol by transesterification, having the abovementioned molecular weights are also suitable. The polyhydroxyl compounds mentioned can be employed as individual components or in the form of mixtures in addition to the polyols of the present invention. These polyols which may be used in addition to the polyols of the present invention are described below by way of example.

15 The mixtures for preparing the TPU or TPUs have to be based at least predominantly on substances which are difunctional in their reaction with isocyanates. The TPUs prepared using these mixtures thus have a predominantly unbranched structure, i.e. they are predominantly not crosslinked.

20 Suitable polyetherols which may, if desired, be used in addition to the polyols (b1) can be prepared by known methods, for example from one or more alkylene oxides having from 2 to 4 carbon atoms in the alkylene radical and, if appropriate, an initiator molecule containing 2 reactive hydrogen atoms in bonded form by anionic polymerization using alkali metal hydroxides such as sodium or potassium hydroxide or alkali metal alkoxides such as sodium methoxide, sodium or potassium ethoxide or potassium isopropoxide as catalysts or by cationic polymerization using Lewis acids such as antimony pentachloride, boron fluoride etherate, etc., or bleaching earth as catalysts. Examples of alkylene oxides are: ethylene oxide, 1,2-propylene oxide, tetrahydrofuran, 1,2- and 2,3-butylene oxide. Preference is given to using ethylene oxide and mixtures of 1,2-propylene oxide and ethylene oxide. The alkylene oxides can be used individually, alternately in succession or as a mixture. Examples of suitable initiator molecules are: water, aminoalcohols, such as N-alkyldialkanolamines, for example N-methyldiethanolamine and diols, such as alkanediols or dialkylene glycols having from 2 to 12 carbon atoms, preferably from 2 to 6 carbon atoms, e.g. ethane-
25 diol, 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol. If desired, it is also possible to use mixtures of initiator molecules. Other suitable polyetherols are the hydroxyl-containing polymerization products of tetrahydrofuran (polyoxytetramethylene glycols). If other polyetherols are used in
30 addition to the polyether polyalcohols (b1) of the present

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invention, preference is given to using polyetherols derived from 1,2-propylene oxide and ethylene oxide, in which more than 50 %, preferably from 60 to 80 %, of the OH groups are primary hydroxyl groups and in which at least part of the ethylene oxide is arranged as a terminal block and in particular polyoxytetramethylene glycols. Such polyetherols can be obtained by, for example, first polymerizing the 1,2-propylene oxide onto the initiator molecule and subsequently polymerizing on the ethylene oxide or first copolymerizing all the 1,2-propylene oxide in admixture with part of the ethylene oxide and subsequently polymerizing on the remainder of the ethylene oxide or, stepwise, first polymerizing part of the ethylene oxide onto the initiator molecule, then polymerizing on all the 1,2-propylene oxide and then polymerizing on the remainder of the ethylene oxide.

The polyetherols, which are essentially linear in the case of the TPUs, have customary molecular weights of from 500 to 10,000, preferably from 600 to 6000 and in particular from 800 to 3500. They can be employed in addition to the polyols of the present invention either individually or in the form of mixtures with one another.

Suitable polyesterols which may, if desired, be used in addition to the polyols (b1) can be prepared, for example, from dicarboxylic acids having from 2 to 12 carbon atoms, preferably from 4 to 8 carbon atoms, and polyhydric alcohols. Examples of suitable dicarboxylic acids are: aliphatic dicarboxylic acids such as succinic acid, glutaric acid, suberic acid, azelaic acid, sebatic acid and preferably adipic acid and aromatic dicarboxylic acids such as phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids can be used individually or as mixtures, e.g. in the form of a succinic, glutaric and adipic acid mixture. Similarly, mixtures of aromatic and aliphatic dicarboxylic acids can be used. To prepare the polyesterols, it may be advantageous to replace the dicarboxylic acids by the corresponding dicarboxylic acid derivatives such as dicarboxylic esters having from 1 to 4 carbon atoms in the alcohol radical, dicarboxylic anhydrides or dicarboxylic acid chlorides. Examples of polyhydric alcohols are alkanediols having from 2 to 10, preferably from 2 to 6, carbon atoms, e.g. ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, 2,2-dimethylpropane-1,3-diol, 1,2-propanediol and dialkylene ether glycols such as diethylene glycol and dipropylene glycol. Depending on the desired properties, the polyhy-

5 drie alcohols may be used alone or in mixtures with one another.

10 Also suitable are esters of carbonic acid with the diols mentioned, in particular those having from 4 to 6 carbon atoms, e.g. 1,4-butanediol and/or 1,6-hexanediol, condensation products of ω -hydroxycarboxylic acids, for example ω -hydroxy-
15 proic acid, and preferably polymerization products of lactones, for example substituted or unsubstituted ω -caprolactones.

20 As polyesterols, preference is given to using alkanediol polyadipates having from 2 to 6 carbon atoms in the alkylene radical, e.g. ethanediol polyadipates, 1,4-butanediol polyadipates, ethanediol-1,4-butanediol polyadipates, 1,6-hexane-
25 diol-neopentyl glycol polyadipates, polycaprolactones and in particular 1,6-hexanediol-1,4-butanediol polyadipates.

30 The polyesterols preferably have molecular weights of from 500 to 6000, preferably from 800 to 3500.

35 c) Suitable chain extenders (c), which usually have molecular weights of less than 500 g/mol, preferably from 60 to 300 g/mol, are preferably alkanediols having from 2 to 12 carbon atoms, preferably 2, 4 or 6 carbon atoms, for example ethanediol, 1,6-hexanediol and in particular 1,4-butanediol and dialkylene ether glycols such as diethylene glycol and dipropylene glycol. However, other suitable chain extenders are diesters of terephthalic acid with alkanediols having from 2 to 4 carbon atoms, for example bis(ethanediol) or bis(1,4-butanediol) terephthalate, hydroxylalkylene ethers of hydroquinone, e.g. 1,4-di(5-hydroxyethyl)hydroquinone, (cyclo)aliphatic diamines, such as 4,4'-diaminodicyclohexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, ethylenediamine, 1,2- and 1,3-propylenediamine, N-methylpropylene-1,3-diamine, N,N'-dimethylthiyledenediamine and aromatic diamines, such as tolylene 2,4- and 2,6-diamine, 3,5-diethyltolylene-2,4- and -2,6-diamine and primary, ortho-dialkyl-, 40 -trialkyl- and/or -tetraalkyl-substituted 4,4'-diaminodiphenylmethanes.

45 Chain extenders which are preferably used are alkanediols having from 2 to 6 carbon atoms in the alkylene radical, in particular 1,4-butanediol, and/or dialkylene glycols having from 4 to 8 carbon atoms.

To adjust the hardn ss and melting point of the TPUs, the molar ratios of the formative components (b) and (c) can be varied within relatively wide ranges. Molar ratios of polyhydroxyl compounds (b) to chain extenders (c) which have been found to be useful are from 1 : 1 to 1 : 12, in particular from 1 : 1.8 to 1 : 6.4, with the hardness and the melting point of the TPU increasing with an increasing diol content.

10 d) Suitable catalysts which, in particular, accelerate the reaction between the NCO groups of the diisocyanates (a) and the hydroxyl groups of the formative components (b) and (c) are the customary catalysts known from the prior art, viz. tertiary amines such as triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylaminocethoxy)ethanol, diisabicyclo[2.2.2]octane and the like and also, in particular, organic metal compounds such as titanate esters, iron compounds such as iron(III) acetylacetone, tin compounds such as tin diacetate, tin dioctoate, tin dilaurate or the dialkyltin salts of aliphatic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate or the like. The catalysts are usually used in amounts of from 0.002 to 0.1 parts per 100 parts of polyhydroxyl compound (b).

25 e) Apart from catalysts, customary auxiliaries and/or additives (e) can also be added to the formative components (a) to (c). Examples which may be mentioned are surface-active substances, foam stabilizers, cell regulators, flame retardants, nucleating agents, oxidation inhibitors, stabilizers, lubricants and mold release agents, dyes and pigments, inhibitors, stabilizers against hydrolysis, light, heat or discoloration, inorganic and/or organic fillers, reinforcing materials and plasticizers.

Further details regarding the abovementioned auxiliaries and
additives may be found in the specialist literature, for example
the monograph by J.H. Saunders and K.C. Frisch "High Polymers",
volume XVI, Polyurethane, parts 1 and 2, Interscience Publishers
1962 and 1964, the abovementioned *Kunststoff-Handbuch*, volume
XII, Polyurethane or DE-A 29 01 774.

40 The thermoplastic elastomers can be prepared by known methods, viz. in the one-shot process continuously on belt units or using reaction extruders and also batchwise in the casting process as well as by the known prepolymer process. In these processes, the components (a), (b) and, if desired, (c) to be reacted can be 45 mixed successively or simultaneously with one another, the reaction commencing immediately.

The reaction is preferably carried out by the one-shot process.

The reactants (a), (b) and, if desired, (c) are preferably used in such a ratio that the ratio of the NCO groups of the component 5 (a) to the sum of all NCO-reactive hydrogen atoms of the components (b) and, if used, (c) is from 1 : 0.9 to 1 : 1.1.2, particularly preferably from 1 : 0.95 to 1 : 1.1, in particular 1 : 1. The reaction is exothermic and usually proceeds rapidly.

10 As has already been mentioned, the reaction mixture comprising (a), (b) and, if desired, (c), (d) and/or (e) can be reacted by the extrusion process or preferably by the belt process. Specifically, in the belt process the procedure is as follows:

15 The formative components (a) to (c) and, if desired, (d) and/or (e) are mixed continuously at temperatures above the melting point of the formative components (a) to (c) by means of a mixing head. The reaction mixture is applied to a support, preferably a conveyor belt, and conveyed through a heated zone. The reaction 20 temperature in the heated zone can be from 60 to 200°C, preferably from 100 to 180°C, and the residence time is generally from 0.05 to 0.5 hours, preferably from 0.1 to 0.3 hours. After the reaction is complete, the TPU is allowed to cool and is subsequently comminuted or granulated.

25 In the extrusion process, the formative components (a) to (c) and, if desired, (d) and (e) are introduced individually or as a mixture into the extruder, reacted at, for example, from 100 to 250°C, preferably from 140 to 220°C, and the resulting TPU is 30 extruded, cooled and granulated.

The processing of the TPUs, which are usually in granule or powder form, is carried out by customary methods. For example, the TPUs are mixed at, for example, from 0 to 200°C, preferably from 35 60 to 150°C and in particular from 80 to 120°C. The mixture can subsequently be homogenized at from 150 to 250°C, preferably from 160 to 230°C and in particular from 180 to 220°C, for example in a flowable, softened or molten state, preferably with degassing, eg. by stirring, rolling, kneading or extruding, for example 40 using a roller apparatus, a kneader or an extruder, and processed to form the desired TPUs. Preferably, the TPUs are introduced as mixtures or individually into an extruder, partially molten at, for example, from 150 to 250°C, preferably from 160 to 230°C and in particular from 180 to 220°C, the mixture is extruded, eg. on a 45 single- or twin-screw machine, for example with degassing, cooled and subsequently granulated. The granules can be subjected to

intermediate storage or be immediately further processed to give the desired products.

The advantages according to the present invention are illustrated 5 by the following examples.

Example 1

Thermoplastic polyurethanes were prepared from 700 parts of MDI, 10 175 parts of butanediol as chain extender (rigid segment content = 39 %) and 1000 parts of a polyether polyol li or lc based on polyoxypolypropylene units and polyoxyethylene units and having the characteristics shown in Table 1 by the known one-shot process.

15 Table 1

| Polyether polyalcohol | li | lc |
|---|-------|------|
| Molecular weight | 1250 | 2000 |
| Hydroxyl number (mg KOH/g) | 90 | 50 |
| 20 Unsaturation [meq/g] | 0.008 | 0.01 |
| Proportion of primary hydroxyl groups (%) | 85 | 75 |
| Proportion by weight of polyoxyethylene units (%) | 20 | 27 |
| Functionality | 1.99 | 1.98 |

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The TPUs prepared using the polyether polyols li or lc have the properties shown in Table 2.

30 Table 2

| TPU sample | Shore hardness A | Density g/cm ³ | Abrasion mm ³ | Tensile strength N/mm ² | Tear propagation resistance N/mm | Elongation at break % |
|-----------------------|------------------|---------------------------|--------------------------|------------------------------------|----------------------------------|-----------------------|
| Polyether polyalcohol | | | | | | |
| li | 90 | 1.16 | 58 | 57 | 63 | 610 |
| 35 lc | 89 | 1.13 | 108 | 20 | 37 | 530 |

30 The TPUs prepared using the polyether polyalcohol component li according to the present invention have significantly improved 40 properties in comparison with the TPUs based on known polyether polyols. The tensile strength, the tear propagation resistance and the elongation at break of the TPUs prepared according to the present invention are significantly increased, while the abrasion was able to be reduced.

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Example 2

Samples of thermoplastic polyurethane incorporating polymer di 1s were prepared from 600 parts of MDI, 140 parts of butanediol (rigid segment content = 30 %) and 1000 parts of polymer diol by the conventional one-shot process, where the diol component is a mixture of the polyether polyol 1i and a polytetrahydrofuran diol (PTHF) having a molecular weight of 1000:

| 10 | Weight ratio of the polyether polyol 1i: PTHF | Shore | Density | Abrasion | Tensile strength | Tear propagation resistance | Elongation at break |
|----|---|------------|-------------------|-----------------|-------------------|-----------------------------|---------------------|
| | | hardness A | g/cm ³ | mm ³ | N/mm ² | N/mm | % |
| 15 | 100:0 | 84 | 1.15 | 86 | 38 | 45 | 610 |
| | 90:10 | 83 | 1.15 | 90 | 42 | 50 | 710 |
| | 80:20 | 84 | 1.145 | 97 | 41 | 48 | 720 |
| | 70:30 | 84 | 1.14 | 81 | 41 | 48 | 740 |
| | 60:40 | 84 | 1.14 | 78 | 46 | 46 | 720 |
| 20 | 50:50 | 84 | 1.135 | 61 | 44 | 50 | 710 |
| | 40:60 | 85 | 1.13 | 54 | 53 | 51 | 670 |
| | 30:70 | 85 | 1.13 | 52 | 56 | 52 | 650 |

It can be seen that thermoplastic polyurethanes which have been prepared using the mixtures of the present invention have excellent properties.

Example 3

30 The mechanical properties of samples of thermoplastic polyurethane incorporating polymer diols, prepared from 600 parts of MDI, 140 parts of butanediol (rigid segment content = 30 %) and 1000 parts of polymer diol, where the diol component used was the polyether polyalcohol 1i according to the present invention or 35 the comparative polyether polyalcohol 1c, were examined. The materials were prepared by the conventional one-shot process, with the temperature being recorded as a function of time during the reaction (Table 4).

40 Table 4

| Time(s) | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 110 |
|---------|----|----|----|----|-----|-----|-----|-----|-----|-----|-----|
| 1i [°C] | 74 | 81 | 87 | 94 | 100 | 106 | 113 | 119 | | | |
| 1c [°C] | 75 | 81 | 86 | 92 | 97 | 102 | 105 | 110 | 114 | 117 | 120 |

The slow temperature rise in the reaction of the comparative polyether polyalcohol clearly shows that the reaction with the component 1c is unsatisfactorily slow. In contrast, the rate at which the reaction temperature increases in the reaction with the 5 component 1i of the present invention shows a desirably rapid reaction from which it can be concluded that conversion is complete even in the preparation of the TPUs by the one-shot process.

10 The mechanical properties of the TPUs are shown in Table 5:

Table 5

| 15 | TPU sample | Shore | Density | Abrasion | Tensile strength | Tear propagation resistance | Elongation at break |
|----|------------|------------|-------------------|-----------------|-------------------|-----------------------------|---------------------|
| | one shot | hardness A | g/cm ³ | mm ³ | N/mm ² | N/mm | % |
| 20 | 3i | 85 | 1.15 | 83 | 39 | 45 | 620 |
| 25 | 3c | 85 | 1.14 | 192 | 20 | 36 | 810 |

20 In addition, the TPUs 3i which were prepared using the polyether polyalcohol 1i according to the present invention have considerably improved mechanical properties. Thus, for example, the abrasion, the tensile strength and the tear propagation resistance are significantly improved in comparison with the TPUs 3c which 25 were prepared using the polyether polyalcohol 1c.

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